Electrical and mechanical properties of plated Ni/Cu contacts for Si solar cells

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Abstract

Plated Ni/Cu/Ag contacts are an industrially feasible metallization approach for high efficiency c-Si solar cells with low surface doping concentrations ($10^{18} \text{cm}^{-3} < N_D < 10^{20} \text{cm}^{-3}$). The 2d-simulations of this work define the minimum requirements on the contact resistivity of metal contacts in a high efficiency solar cell design. The following experimental study of the contact resistivity of plated Ni/Cu/Ag contacts on lowly doped phosphorus emitter demonstrates low contact resistivities in the m$\Omega$cm$^2$ regime, which enable solar cells with high fill factors. Furthermore, the paper analyzes the influence of the thermal silicidation process on pseudo-fill factor losses and on the mechanical contact adhesion. The contact adhesion is also studied with respect to the laser contact opening process. The results of this work demonstrate that the right choice of back-end processes enable plated Ni/Cu/Ag contacts with low contact resistivities in combination with high contact adhesions above 1 N/mm.

1. Introduction

The replacement of Ag screen printing with Ni/Cu plating is a promising approach to reduce the material costs for metallization processes in various solar cell designs. The successful application of plated Ni/Cu contacts was recently demonstrated for various kinds of p-type [1,2] and n-type [3] silicon solar cells. Generally, metallization...
processes for next generation solar cell concepts face new challenges in terms of reaching low contact resistances for small contact areas on ultra-lightly doped emitters ($N_D << 10^{20} \text{ cm}^{-3}$). Furthermore, the module integration of all solar cell designs requires a metallization process which is not only able to achieve high solar cell efficiencies but also provides metal contacts with good solderability and sufficient contact adhesion. The challenging task of sufficient contact adhesion of plated Ni/Cu/Ag contacts was one of the main concerns, which hindered the introduction of plated Ni/Cu/Ag metal contacts in the mass production of silicon solar cells in the past. Although, there was already a successful transfer of a Ni/Cu based metallization from the microelectronics industry into the PV market by BP Solar [4] it was still challenging to develop a simplified process that meets today’s need for cost reduction. One of the most promising technology routes for the replacement of screen printed Ag contacts by plated Ni/Cu metallization is the application of laser micro-structuring of the passivation layer to mask the metal deposition. Recent publications demonstrated not only high solar cell efficiencies but also sufficient contact adhesion for module fabrication using soldered cell interconnection [2,5].

In the following, laser defined and plated Ni/Cu/Ag contacts are analyzed by a simulation and two experimental studies. The first section gives a theoretical background of the minimum requirements in terms of contact geometry, contact recombination and contact resistivity of front side metal contacts using 2d-simulations of high efficiency passivated emitter and rear locally diffused solar cells (PERL). These requirements are compared with an experimental study on the contact resistivity of plated Ni contacts as a function of the phosphorus surface doping concentration. The last section analyzes the influence of laser process induced surface roughness and the application of a silicidation anneal on the contact adhesion of plated Ni/Cu/Ag contacts. The results of this work demonstrate that the right choice of back end processes/parameters results in well adhering metal contacts with electrically excellent properties in terms of contact resistivity and leakage currents, which would allow conventional string fabrication and reliable module integration of high efficiency Si solar cells.

Fig. 1: Simulated (EDNA) saturation current densities of passivated $J_{01,\text{pas}} (S_0 = S_0(N_D))$ and metallized $J_{01,\text{cont}} (S_0 = 10^7 \text{ cm/s})$ n-type emitters with Gaussian doping profile and their corresponding sheet resistance. The red circle represents the emitter profile for the following 2-d simulations.

2. Theoretical considerations on electrical contact properties for high efficiency Si solar cells

The achievement of high solar cell efficiencies $\eta > 22\%$ requires a significant reduction of the different power losses, which are limiting state-of-the-art industrial Si solar cells [6]. The key aspects are the reduction of the recombination and series resistance losses described by the parameters $J_{01}$ (dark saturation current density) and $R_s$ (series resistance). Looking at the front side of a PERL solar cell, the recombination losses of the front side emitter can be reduced by introducing an ultra-lightly doped emitter. Fig. 1 shows EDNA [7] simulations that demonstrate the reduction of the saturation current density $J_{01,\text{pas}}$ with decreasing emitter depth and surface doping density of a passivated n-type emitter with Gaussian doping profile. The dependency of the surface recombination velocity on the surface doping concentration was taken into account by applying the parameterization of the data of Glunz et al.
Although, \( J_{01,\text{pas}} \) is decreasing for decreasing emitter doping densities the saturation current density in the contacted region \( J_{01,\text{cont}} \) is increasing. Therefore, the overall improvement due to a decrease of \( J_{01,\text{pas}} \) has to be assured by low contact fractions in order to reduce the impact of increasing \( J_{01,\text{cont}} \) on the solar cell performance. This illustrates the demand for narrow front side contact widths for solar cells with ultra-lightly doped emitters.

![Table 1. Simulation parameters](image)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simulation</td>
<td>Quokka 2.2, 2D unit cell</td>
</tr>
<tr>
<td>Si material</td>
<td>p-type Si, 190μm, 1.5 Ωcm, 2.5 ms</td>
</tr>
<tr>
<td>Front contact</td>
<td>1.3mm pitch, ( \rho_{\text{cont}} = 10^{-3} , \text{Ωcm}^2 ) or variable, ( J_{01,\text{cont}} = 1164 , \text{fA/cm}^2 ) or variable</td>
</tr>
<tr>
<td>Rear contact</td>
<td>1.3 mm pitch, 20 μm LCO width</td>
</tr>
<tr>
<td>Emitter</td>
<td>( R_{\text{sheet}} = 149 , \Omega/sq., J_{01,\text{pas}} = 65 , \text{fA/cm}^2 )</td>
</tr>
<tr>
<td>Rear</td>
<td>( J_{01,\text{pas, rear}} = 30 , \text{fA/cm}^2 ), ( J_{01,\text{cont, LBSe}} = 400 , \text{fA/cm}^2 )</td>
</tr>
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Fig. 2 Simulated solar cell efficiencies of p-type PERL solar cells depending on the front side contact width and the contact resistivity.

To analyze the impact of a decrease of the contact width on contact resistance limitations of the solar cell efficiency we conducted an exemplary 2d-simulation of a PERL solar cell with an ultra-lightly doped emitter using the simulation tool Quokka [10]. The applied emitter profile is marked in Fig. 1 and features a Gaussian profile with a sheet resistance of 149 Ω/sq., a pn-junction depth of 0.5 μm and a surface doping concentration of 2 x 10^{19} cm^{-3}. This results in a saturation current density of about 65 fA/cm² for passivated (\( S_0 = 8000 \, \text{cm/s} \)) and 1164 fA/cm² for metallized surfaces (\( S_0 = 10^7 \, \text{cm/s} \)). The other simulation parameters are listed in Table I. Fig. 2 shows the case of a contact resistance limited solar cell design where the front side metal contact resistivity limits at some point for decreasing contact width the solar cell efficiency. The simulation demonstrates that contact resistivities in the low mΩcm²-regime are necessary to enable high solar cell efficiencies by decreasing the front side contact width.

3. Experimental setup

Two different kinds of samples were investigated in this work. Test samples for the evaluation of the contact resistivity and solar cells featuring a laser defined and plated front side metallization for contact adhesion measurements. The measurement of the contact resistivities of plated Ni/Cu/Ag metal contacts was performed on samples with the processing scheme shown in Fig. 3 a). The contact resistivity was measured by using the transfer length method (TLM). The samples featured different ion-implanted phosphorus emitters with varying surface dopant concentrations \( N_{d,\text{surf}} \) in the range of \( 10^{18}-10^{20} \, \text{cm}^{-3} \), which were passivated by a thin PECVD SiNx ARC/passivation layer. The SiN\(_x\) layer was locally removed in a TLM pattern via pulsed UV laser ablation (\( \tau_{\text{pulse}} \leq 15 \, \text{ps}, \lambda = 355 \, \text{nm} \)) and subsequently locally metallized via light induced plated (LIP-Ni) Ni (only thin seed layer), LIP-Cu and a thin LIP-Ag capping. The TLM pattern defined via local laser ablation featured LCO widths of about 20 μm and contact length of 10 mm. A dicing saw was used to isolate the emitter between each TLM pattern. The contact resistivity was calculated by the transfer length method using 4-point probe IV-measurements at various contact combinations with varying contact distance.

Al-BSF solar cells with a process scheme shown in Fig. 3 b) were used to analyze the influence of silicidation effects on electrical (contact resistivity, silicidation induced pFF degradation) and mechanical (contact adhesion) aspects of the plated metal contacts. Commercial Al-BSF solar cell precursors were used, featuring a shallowly
(200-300 nm) diffused phosphorus emitter with a surface doping concentration of about 2-3 \times 10^{20} \text{ cm}^{-3}. All samples were laser patterned resulting in a 3 busbar (BB) contact grid design with contact opening widths in the range of 20-30 \mu m and finger pitch of 1.3 mm. The laser patterning was divided into three groups featuring UV laser ablation with nanosecond ($\tau_{\text{pulse}} \leq 25 \text{ ns}$, $\lambda = 355 \text{ nm}$, LCO 1) and picosecond ($\tau_{\text{pulse}} \leq 15 \text{ ps}$, $\lambda = 355 \text{ nm}$, LCO 2) laser pulses or laser contact openings using laser chemical processing (LCP) with green ($\tau_{\text{pulse}} \leq 70 \text{ ns}$, $\lambda = 532 \text{ nm}$) nanosecond laser pulses coupled into a liquid jet. All laser processes featured roughly the same laser pulse density [11]. After laser patterning, fast firing (FFO) for Al-BSF formation on the rear side and single side HF-pretreatment of the front side, the metal contacts were plated in subsequent Ni-LIP, Cu-LIP and Ag-LIP processes. After plating, a part of the samples were not annealed while another part was annealed with a variety of processing conditions in an inline furnace aiming the silicidation of the Ni-Si interface. After silicidation the samples were IV-tested to characterize possible pFF-degradation and soldered to perform peel tests of the plated metal contacts. The peel testing was performed under an angle of 90° to the contact, while the Al rear side of the solar cells was glued onto a glass substrate in order to measure the contact fraction force and to avoid lowered peel forces due to wafer breakage below the contacts. Furthermore, local emitter windows were created via dicing saw emitter isolation in order to measure the contact resistivity via 4-point probe TLM measurements.

Fig. 3 Process scheme of a) sample type A and b) sample type B for the following electrical and mechanical analysis.

4. Results & discussion

4.1. Contact resistivity

The contact resistivity of laser defined plated Ni/Cu/Ag contacts (sample type A) was measured and is shown in Fig. 4 for varying phosphorus surface doping densities without silicidation anneal (blue solid squares). The comparison of the contact resistivity before (blue solid triangles) and after (blue open triangles) the silicidation anneal was measured using sample type B (blue triangles). The measured data of this work are compared to the theoretical contact resistivity (black lines, including thermionic emission, thermionic field emission and field emission as a function of the surface doping concentration for different Schottky-barrier heights), experimental values for PVD/plated Ni or Ni-silicide layers from the literature (orange data) and experimental values for screen
printed Ag contacts (green data). The experimental results of this work (blue data) in Fig. 4 demonstrate the ability of plated Ni to contact lowly doped emitters. The TLM measurements demonstrate that even for ultra-lightly doped emitters similar to the assumptions in section 2 the contact resistivity is in the low μΩcm² or below for surface doping densities down to 1 x 10¹⁹ cm⁻³. The comparison to state-of-the-art screen printed Ag contacts reveals increasing benefits of plated Ni contacts in terms of contact resistance for decreasing surface doping concentrations. The application of a silicidation anneal (blue open triangles) results in a further decrease of the specific contact resistivity. The comparison of the contact resistivities for different annealing conditions (not shown here) shows no significant differences for the applied annealing variation.

4.2. Silicidation-induced pFF degradation

As discussed in more detail in [12–15] the thermal silicidation of laser patterned and plated Ni/Cu/Ag contacts bears the risk of pFF degradation due to the growth of locally deep silicide spikes. Fig. 5 illustrates the measured pFF of sample type B (only LCO 2) before and after silicidation. The data is plotted as a function of the theoretical silicidation depth (silicidation depth in cm) \( W_{Ni_2Si+NISi} \) using the model of Coe et al. [16]. The theoretical silicidation depth is a function of the applied annealing temperature profile \( T(t) \), the total annealing time \( t_e \), the elementary charge \( q \) and the Boltzmann constant \( k_B \). The model of Coe includes the most relevant silicidation phases in the applied temperature regime of 250-400°C.

\[
W_{Ni_2Si+NISi} = \frac{1}{t_e} \int_0^{t_e} t \left( 10^3 e^{\frac{-14q}{k_B T(t)}} \right) + \sqrt{t \left( 10^{-2} e^{\frac{-13q}{k_B T(t)}} \right)} dt
\]  

(1)

Although, the theoretical silicidation depth is a quantity to compare the influence of different annealing conditions on the silicidation process the absolute value of \( W_{Ni_2Si+NISi} \) represents the ideal silicide depth. Previous
publications already demonstrated that especially for samples with laser defined contact openings and plated Ni contacts the silicide growth can be non-homogeneous \cite{15,12}. Therefore, the absolute value of the silicidation depths on the analyzed samples may differ with an offset from $W_{NiSi+N_{NiSi}}$ but the annealing dependent trends should be given correctly. Cross section analyzes of the contact interface revealed for most samples of type B very low amounts of Ni silicide growth. However, the results in Fig. 5 demonstrate the strong dependency of the pFF on the applied silicidation anneal. Increasing thermal budget results in lower pFF. Similar to previous publications \cite{12} this indicates the presence of locally deep silicides rather than homogeneously deep silicides. The origin of locally deep silicides is most likely regions with increased diffusion rates especially at local crystal defects, e.g. laser-induced crystal defects. In the case of short and low temperature anneals with theoretical silicide depths lower than 10 nm the measured pFF degradation is below the data spreading in the performed experiment and demonstrates that even for shallow emitter depths the combination of LCO and plated Ni/Cu/Ag contacts can result in stable pFF for optimized back-end processes.

![Graph showing measured pFF as a function of theoretical silicide depth.](image)

Fig. 5 Measured pFF as function of the theoretical silicide depth of sample type B (degraded Al-BSF solar cell) with process groups without silicidation and with varying thermal silicidation processes. Please note the discrete x-axis of the theoretical silicide depth.

### 4.3. Micro-morphology related contact adhesion

The influence of the micro-morphology related contact adhesion is analyzed by optical and electron microscope measurements in different processing states in combination with peel force measurements (90° peel force angle, soldered junction to the interconnection ribbon) of the sample type B (LCO 1, LCO 2, LCP).

![Graph showing measured max. and median peel forces.](image)

Fig. 6 Measured max. and median peel forces (normalized by BB width, 1.5 mm, 90° pulling angle) of non-annealed sample type B.

The results in Fig. 6 demonstrate the crucial influence of the laser patterning process of the passivation/ARC layer on the contact adhesion of the plated metal contact. LCO 1 (blue data) results in no significant contact adhesion with
median and maximum peel forces below 0.1 N/mm and 0.2 N/mm, respectively. The results for samples with LCP (orange data) patterned contact openings show slightly larger median and maximum peel forces of 0.2 N/mm and 0.3 N/mm. The samples with LCO 2 (green data) demonstrate significantly larger mean peel forces of 0.6 and 1.3 N/mm for the median and maximum peel force. The finding of significantly larger peel forces for plated contacts with ps-laser definitions in comparison to ns-laser defined LCO is in agreement with the findings of Bay et al. [5].

To further investigate the crucial influence of the LCO process before plating the contact interface after the laser process was analysed by optical and scanning electron microscope (SEM) measurements shown in Fig. 6. Fig. 7 a) displays optical microscope measurements in top view of the LCO contact geometry in the BB region after the different laser processes of sample type B. The applied laser parameters featured no spatial pulse overlap of the laser pulses, which results in laser structures with opening fractions below 100% in the BB region and for the LCP samples in a non-homogeneous contact opening. The optical contact opening fraction is in a similar range for LCO 1.
and LCO 2 but about 20% abs. lower for LCP. In Fig. 7 b) the micro-morphology of the laser ablation process is shown in SEM measurements in top view after LCO. The comparison of ns-laser ablation (LCO 1) and ps-laser ablation (LCO 2) reveals in both cases laser interference patterns [27] at the pyramid faces. However, melt movement-induced smoothening of the surface results in lower surface roughness for ns-laser pulses (LCO 1). Furthermore, LCO 1 features ball shaped Si melt movement at the pyramid tips. The surface of LCO 2 shows increased surface roughness due to filigree structures at the pyramid faces. Similar results were shown by Bay et al. [5]. The surface topography of the LCP sample features no interference pattern due to laser intensity inhomogeneities in the liquid jet [28] but still shows an increased surface roughness compared to LCO 1. The increased surface roughness origins most likely due to the combination of liquid jet-induced laser intensity inhomogeneities and liquid jet-induced melt movements. The SEM analysis of the LCO morphology after plating, soldering and peel test in the BB region and the interconnection ribbon is shown in Fig. 7 c) and d), respectively. All laser processes show the same amount of ripped out Si at the pyramid tips of the BB, which is still visible at the interconnection ribbon. Furthermore, the surface roughness at the pyramid faces seems to be slightly smoothened for all laser processes but is still visible at the BB. The comparison of the peel force results in Fig. 6 and the contact geometry and micro-morphology in Fig. 7 reveals a correlation between the resulting LCO topography at the pyramid faces and the resulting peel force. Increasing topography (LCO 1 $\rightarrow$ LCP $\rightarrow$ LCO 2) leads to increasing peel force. This effect becomes more evident by taking into account the contact opening fraction after laser processing. The comparison of LCO 1 and LCP reveals larger peel forces for the LCP samples even though the laser contact opening fraction in the BB region is significantly lower than in the case of LCO 1 with lower peel forces.

It is worth to note that the ripped out pyramid tips show no correlation to the peel force results. Although, the peel force results show significant differences for the different laser processes, the amount of ripped out pyramid tips is similar in all cases. It is not surprising that the Si fracture appears most likely at the pyramid tip, but it could also be supported by increased laser induced crystal damage at these positions due to laser focusing at the pyramid tip [27]. The missing correlation of peel force and ripped out pyramid tips also leads to the hypothesis that low opening fraction LCO formation, e.g. ARC removal only at the pyramid tips is not sufficient for adequate peel forces of the plated metal contacts. This hypothesis has to be investigated in future experiments, which also need to take into account possible decreases of the adhesion force due to laser induced crystal damage.

![Graphs and Images](image-url)
4.4. Silicidation related contact adhesion

Various publications [29,30] show that the formation of Ni-silicide at the contact interface can significantly increase the contact adhesion of (plated) Ni contacts on planar or textured Si surfaces. Fig. 8 shows the measured peel force of sample type B with optimized LCO 2 and the corresponding surface topography of the BB region after peel testing. The peel test measurements in Fig. 8 a) show increased contact adhesion after the silicidation anneal, which correlates with large ripped out Si chunks in the SEM investigations shown in Fig. 8 b). The sample without anneal in Fig. 8 c) shows only minor parts of ripped out Si, which are also mostly located at the pyramid tips, similar to the SEM study of Fig. 7. Cross section studies (not shown here) of sample type B after silicidation anneal at positions of ripped out Si reveal no significant amount of Ni-silicides at the Ni-Si interface. This leads to the assumption that the applied back end processes result only in very localized silicide formation. However, even the localized silicide growth seems to be sufficient to significantly increase the contact adhesion of the plated contact.

5. Conclusion

The electrical and mechanical requirements for metal contacts of c-Si solar cells with ultra-lightly doped emitters are analyzed in 2d-simulations and compared to experimental studies of the electrical and mechanical contact properties. The performed 2d-simulations demonstrate the demand for metallization approaches with narrow contact width in combination with low contact resistivities in order to enable solar cell efficiencies above 22%.

The combination of laser micro-structuring (LCO) of the passivation layer for contact definition and subsequent Ni/Cu/Ag plating enables an industrially feasible approach, which fulfills both requirements. The application of commercial state-of-the-art LCO systems allows LCO structuring widths in the range of 10-30 μm, which result in plated contact widths of 20-40 μm. The 2d-simulation results show that for these geometries a contact resistivity well below $10^{-2}$ Ωcm$^2$ is desirable. The TLM study of this work with laser defined plated Ni/Cu/Ag contacts demonstrates the ability of this metallization approach to achieve contact resistivities much below this threshold even for phosphorus surface doping densities down to $10^{19}$ cm$^{-3}$. Furthermore, it is shown that the application of a thermal silicidation anneal can further decrease the contact resistivity. The results of this work demonstrate that even commercially available Al-BSF solar cells with shallow emitter diffusions are suitable for thermal silicidation without significant pFF degradations. The analysis of the contact adhesion of plated Ni/Cu/Ag contact with different LCO contact definitions reveals the strong dependency on the LCO process. The combination of peel testing (90° peel force angle) and SEM micro-characterization reveals a correlation of the measured peel force and increased surface roughness within the contact opening after LCO processing. Only LCO processes with picosecond laser pulses resulted in sufficient peel forces of up to 2 N/mm and 0.7 N/mm in maximum and median, respectively. The application of a subsequent thermal silicidation anneal after plating can further increase the contact adhesion leading to peel forces of about 4 N/mm and 1.2 N/mm in maximum and median, respectively. The results of this work demonstrate that the right choice of back end processes/parameters results in reliable metal contacts, which allow conventional string fabrication and reliable module integration of high efficiency Si solar cells. Even back-end processing without thermal annealing after plating resulted in this experiment in high contact adhesion. However, the introduction of a rapid thermal anneal in the temperature range of 250-400°C can improve the contact resistivity as well as the contact adhesion.

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